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I.R. STUDY OF ALKYL-AMMONIUM VERMICULITE COMPLEXES

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Abstract—Two octyl-ammonium vermiculite complexes with different 001 periodicities have been studied by i.r. spectroscopy. In each case i.r. spectroscopy affords information on the orientation of the $-NH_3^+$ groups and the strength of the hydrogen bond between these groups and the silicate oxygen surfaces. Also a perturbation of the vibration of the OH groups of the silicate has been observed that seems to be related to the distance from the center of the layer at which the $-NH_3^+$ groups are situated.

The i.r. results are discussed in relation to the structural models deduced from X-ray analysis.

INTRODUCTION

THE GEOMETRY and mechanism of interaction between organic molecules and layer silicates is not yet fully understood. For neutral molecules, it is becoming increasingly evident that a predominant role is played by the inorganic exchangeable cations in the sorption mechanism with the formation of true coordination compounds. For organic cations, an exchange reaction occurs and the association involves electrostatic attraction between the negative layers of the silicates and the positive part of the organic compound. In this case, other types of association, such as hydrogen bonding with the basal oxygen atoms, can also be present.

The normal procedure for studying these organic complexes has been by X-ray diffraction. In many analyses the molecules of ions are only fitted in the available space, according to their dimensions. In a few other cases, a more complete structure analysis has been attempted, but in each, imperfection of the crystal left some uncertainty as to the location of the individual atoms (Haase, Weiss, and Steinfink, 1963).

I.R. spectroscopy has been found very useful in the study of clay-organic interactions (Fripiat *et al.* 1962; Serrotosa, 1965, 1968; Farmer and Mortland, 1966). The type of association can be deduced from the perturbation of the adsorption frequencies of the organic molecules, and the orientation of the molecules can be determined from the change in intensity of specific bands when the incidence angle is varied.

This paper is concerned with an i.r. study of alkyl-ammonium complexes of vermiculite, in order to investigate the orientation of the ions and the role of hydrogen bonding in the association. Considerable attention has been given to these complexes by Weiss (1963) and recently by Walker (1967) and by Johns and Sen Gupta (1967) who made a one-dimensional structure analysis of a series of alkyl-ammonium complexes, including the ones studied in this paper.

EXPERIMENTAL

The sample used in this investigation was the iron-free trioctahedral vermiculite from Llano Co., Texas. From the natural sample, individual single crystals were selected and monitored by X-ray diffraction. Any flake exhibiting mica peaks was discarded. The selected Mg-vermiculite flakes were placed in a flask containing 1N NaCl. The flask was covered with a watch glass and placed in the oven at 70°C. The NaCl solution was changed every 12 hr. The exchange of Mg by Na was monitored by X-ray diffraction. The Na-vermiculite gives a two layer complex with a 14·8 A spacing. At low relative humidity (below 50 per cent) a one-layer complex is stable with a spacing of 11·8 A, permitting easy check of the extent of the exchange. After 2 days the exchange was completed. The Na-vermiculite flakes were placed in a 1N solution of *n*-propyl-amine hydrochloride at 70°C, which was changed every 12 hr. After the exchange was completed, as indicated by a series of basal reflections related to an 18·2 Å periodicity, the *n*-propyl-ammonium vermiculite

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was washed with water to remove the excess of salt. The *n*-propyl-ammonium vermiculite has the ability to disperse in water and from the suspension, films (4–5 mg/cm^2) were prepared by filtration through a micro-pore filter. When dried, the films were separated from the support and converted in the octyl-ammonium form by immersing them in octyl-amine hydrochloride solution at 70°C. The progress of the reaction was monitored by removing the film from the solution and examining the (00l) X-ray reflections. The reaction was considered complete when a rational series of (00l) reflections was obtained that did not change with further reaction.

The i.r. spectra were recorded on a Beckman IR-7 i.r. spectrophotometer at two angles of incidence, 0° and 40°. Two kinds of complexes were obtained:

(a) The fully expanded phase, obtained by repeated treatment with 1N solution of octyl-amine hydrochloride and washing a few minutes in water to remove the excess of salt. This complex has a sequence of ordered (001) reflections related to a 28·1 A periodicity.

(b) The collapsed phase, obtained by washing the expanded complex several times with water at 70°C and drying it in an oven at 65°C. The d_{001} value of this complex is 19·0 A.

According to Johns and Sen Gupta (1967), the compositions of these two complexes can be represented as:

$[Mg_6Al_2Si_6O_{20}(OH)_4]^{-2\cdot00+}[H_3N\text{-alkyl}]_2\,2\,\text{alkyl-}NH_2$

fully expanded phase.

$[Mg_6Al_2Si_6O_{20}(OH)_4]^{-2\cdot00+}[H_3N\text{-alkyl}]_2$

collapsed phase.

Figures 1 and 2 show schematically the structures of these two complexes.

RESULTS AND DISCUSSION

Information about the structure of these complexes has been obtained from the study of the i.r. spectrum of the interlayer octyl-ammonium ions and also from the perturbation of the vibration of the structural OH groups of the silicate layer.

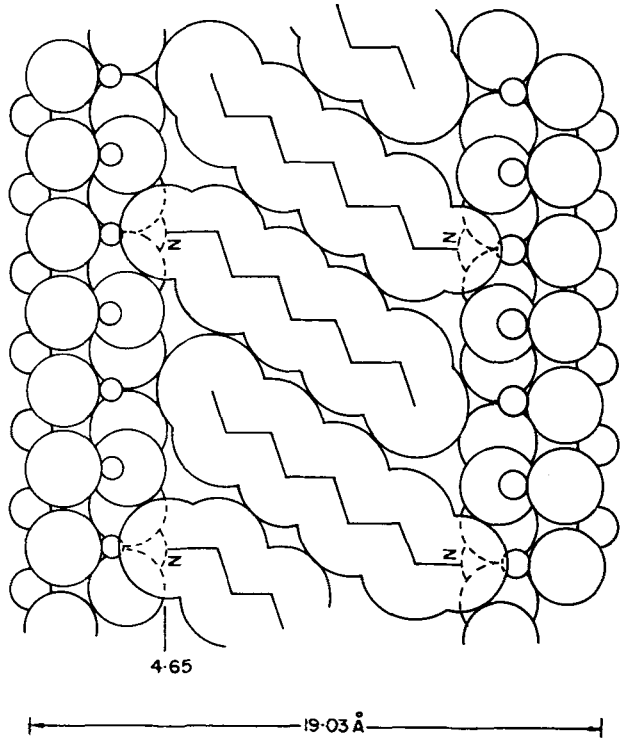


Fig. 1. Structure of the octyl-ammonium-vermiculite complex (collapsed phase, 19·0 A) after Johns and Sen Gupta (1967).

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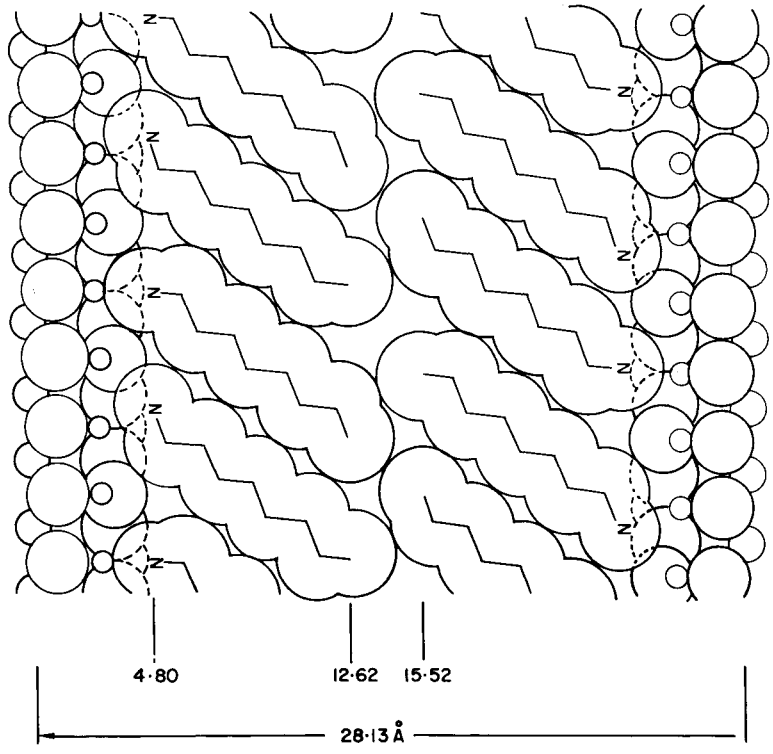


Fig. 2. Structure of the octyl-ammonium-vermiculite complex (fully expanded phase, 28·1 A) after Johns and Sen Gupta (1967).

I.R. study of the octyl-ammonium ions

The i.r. spectra of the two complexes (Fig. 3) show the characteristic bands corresponding to the CH_3, CH_2, and NH_3^+ groups.

The CH_3 groups give bands at: 2975–2950 cm^{-1}, asymmetric C—H stretching; 2885–2860 cm^{-1}, symmetric C—H stretching; 1470–1435 cm^{-1}, asymmetric C—H bending; and 1385–1370 cm^{-1}, symmetric C—H bending.

The CH_2 groups produce bands at 2940–2915 cm^{-1}, asymmetric C—H stretching; 2870–2845 cm^{-1}, symmetric C—H stretching; 1480–1440 cm^{-1}, scissoring; ~ 720 cm^{-1}, rocking and others having positions that are not so well established, corresponding to the twisting and wagging vibrations.

The $-NH_3^+$ groups give adsorption at about 3200–3100 cm^{-1}, corresponding to the N—H stretching vibrations, and at 1600 cm^{-1} and 1580–1500 cm^{-1} that are associated with the asymmetrical and symmetrical $-NH_3^+$ deformation vibrations respectively. The symmetrical $-NH_3^+$ deformation vibration (class A_1) consists of the symmetric extension of the base of the tetrahedron and the change in dipole moment is along the perpendicular to this base (C_3 axis). The asymmetrical deformation vibration involves a tangential displacement of the hydrogen atoms; this is a degenerate vibration of class E and the change in dipole moment is parallel to the base of the tetrahedron. The effect of hydrogen bonding shifts these two deformation bands to higher frequencies. The direction of the band shift of these bending modes is opposite to that of stretching modes. A study of these bands in a series of amine inorganic coordination complexes (Svatos *et al.* 1957) has shown that the $-NH_3^+$ symmetric deformation frequency is more sensitive to hydrogen bonding than the asymmetric one. This result could be explained by the conclusions drawn from normal coordinate analysis (Mizushima, 1955).

The differences between the infrared spectra of the two complexes studied are mainly related to the absorption corresponding to the symmetric deformation vibration of the $-NH_3^+$ group. This band appears in the region between 1500 and 1580 cm^{-1}.

In the collapsed complex, this band is present at higher frequency (1570 cm^{-1}), and shows a

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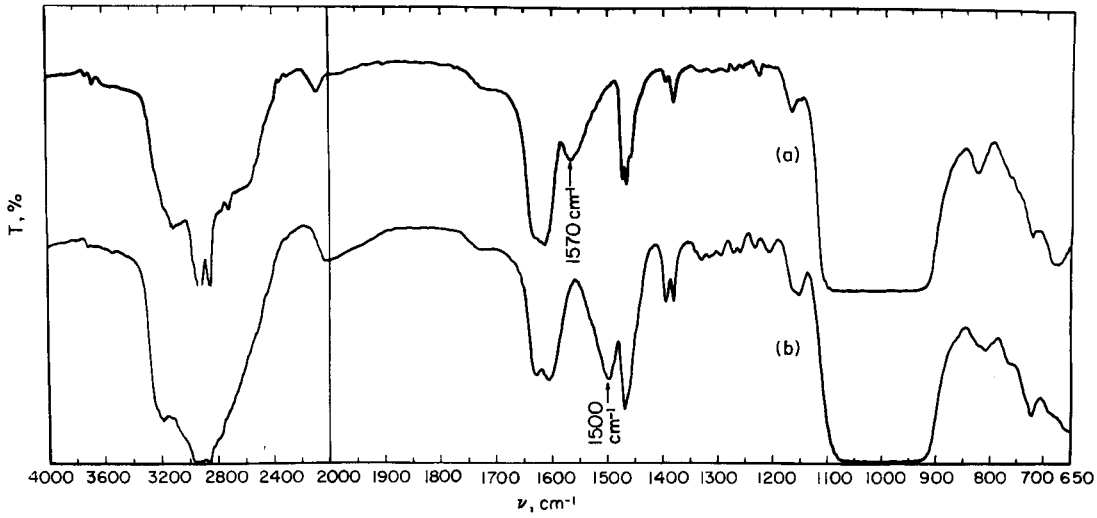


Fig. 3. I.R. spectra of the octyl-ammonium vermiculite complexes (film with 0° incidence): (a) collapsed phase (b) fully expanded phase. In the figure are indicated the position of the bands corresponding to the symmetric deformation vibration of the $-NH_3^+$ groups: 1570 cm^{-1} in the collapsed complex and 1505 cm^{-1} in the fully expanded complex.

significant increase in absorption with the incidence angle (Fig. 4). The position of the band indicates a strong hydrogen bond and the pleochroism indicates a disposition of the $-NH_3^+$ with its C_3 axis, that is, the N—C bond, perpendicular to the silicate layers. This is in agreement with the proposed model derived from X-ray analysis (Fig. 1).

For the fully expanded complex, the band appears at lower frequency (1505 cm^{-1}), and does not show significant increase in absorption with the incidence angle (Fig. 5). These results indicate weaker hydrogen bonding and an orientation of the $-NH_3^+$ group more parallel to the silicate layers.

Johns and Sen Gupta (1967) assumed, for this expanded phase, the neutral octylamine molecules, produced by hydrolysis of the hydrochloride, are intercalated between the octylammonium ions. Two different orientations of the molecules and ions are involved, half of them have their C—N bond essentially perpendicular to the silicate layer and the other half highly inclined to it (Fig. 2). From X-ray diffraction analysis, it is not possible to make a specific assignment of either orientation to the ions or to the neutral molecules.

The i.r. study does not permit a positive confirmation of the existence of neutral molecules, because their absorption bands appear at about the same positions as those of the octylammonium ions. The alkyl-amines are characterized by an absorption at about 1620 cm^{-1}, corresponding to the scissoring vibration of the $-NH_2$ group. This band is at about the same frequency as the asymmetric deformation vibration of the $-NH_3^+$.

In the spectrum of the fully expanded complex (Fig. 5) two distinct bands are observed in this region, at 1630 and 1605 cm^{-1}. These can be assigned to the $-NH_2$ and $-NH_3$ groups respectively if we note that in general the NH_2-scissoring occurs at higher frequency than the NH_3^+-asymmetric deformation. If this assignment is correct, the increase in intensity with increased incidence angle of the 1630 cm^{-1} band can be interpreted to indicate that the $-NH_2$ groups have their axes normal to the silicate layer. Therefore, the neutral molecules are those disposed with the N—C bond normal to the surface. However, the existence of two bands in this region of the spectrum can also be explained by the splitting of the degenerate asymmetric deformation vibration of the $-NH_3^+$ group due to the lowering of the symmetry as a consequence of unequal hydrogen bonding of the three N—H bonds.

Perturbation of the vibration of structural OH groups

Indirect evidence for the disposition of the interlayer ions can be drawn from the perturbation of the vibration of the structural OH groups of the silicate layer by the interlayer organic ions.

As has been shown by Serratosa and Bradley (1958), the orientation of the OH bond axis depends on the occupancy of the octahedral sheet. In dioctahedral compositions in which only two-

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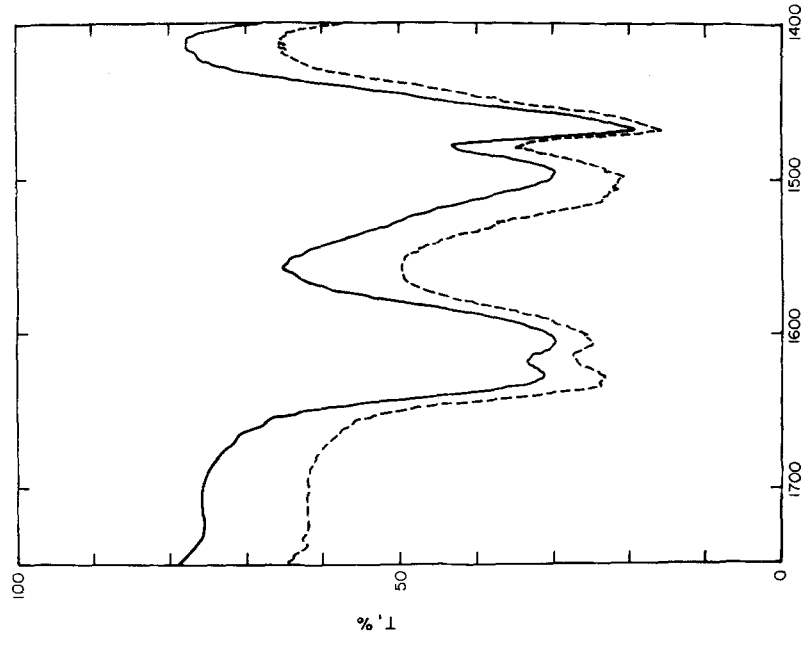


Fig. 5. I.R. spectrum of the fully expanded octyl-ammonium complex for two angles of incidence (– – – 0° and – – – 40°). The symmetric deformation frequency is situated at 1505 cm^{-1} and does not show a significant increase with the incidence angle.

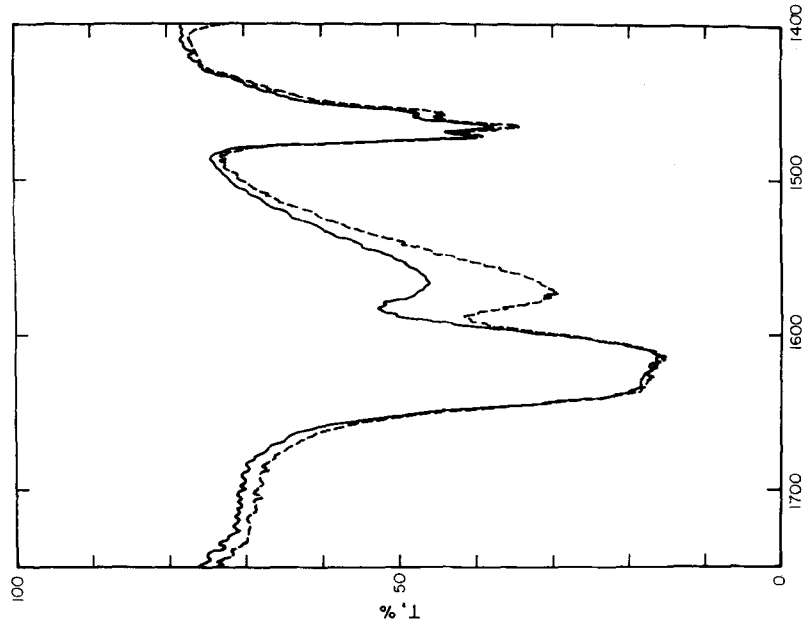


Fig. 4. I.R. spectrum of the collapsed octyl-ammonium complex for two angles of incidence (– – – 0° and – – – 40°) showing the directional dependence of the symmetric deformation band of the $-NH_3^+$ group (1570 cm^{-1})

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thirds of the octahedral positions are occupied, the OH bond axes lie at a small angle to the plane of the layers, probably pointing to the octahedral vacancies. The absorption band is present at 3620 cm^{-1}. In trioctahedral compositions, all the octahedral positions are occupied and the O—H bonds are perpendicular to the silicate layers, pointing to the hexagonal (trigonal) hole of the silica sheet. In this disposition the OH are free of hydrogen bonding, but are somewhat perturbed by the presence of interlayer cations (in micas) and absorb at higher frequencies (~ 3700 cm^{-1}).

The frequency at which the OH bonds absorb is also modified by the nature of the ions in octahedral positions (Vedder, 1964). In general, the substitution of Mg by Fe in trioctahedral compositions, shifts the band to lower frequencies.

Farmer and Russell (1966) have reported studies of the perturbation of the OH vibration by the interlayer ions. Because these ions are positively charged, they produce an increase in the stretching vibration frequency of the OH's (shift in the opposite direction to that produced by hydrogen bonding). The frequency shift must be related to the charge of the interlayer cation and to the OH-cation distance, that is to the penetration of the cation into the hexagonal (trigonal) hole.

The Llano vermiculite is a trioctahedral mineral essentially free of iron with all the octahedral positions occupied by Mg. In the structure with similar octahedral composition but without interlayer ions (talc), the unperturbed OH stretching vibration produces a band at 3680 cm^{-1}. This is also the only frequency observed in the Llano vermiculite when the interlayer ions are separated from the silicate layers by water molecules (hydrated Mg and Na vermiculite). As the water is removed a new band appears at higher frequency. This band represents the OH whose vibration is perturbed by the interlayer cations countersunk in the hole.

In the octyl-ammonium complexes (Fig. 6)

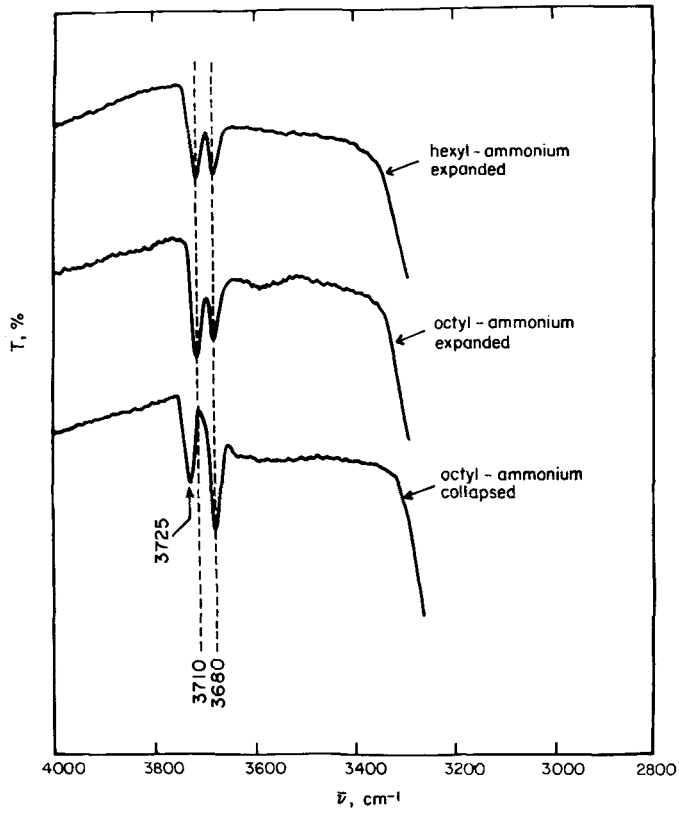


Fig. 6. I.R. spectra of octyl-ammonium complexes in the OH region for inclined incidence (40°). The two observed frequencies represent the unperturbed (3680 cm^{-1}) and perturbed (high frequency) structural OH groups. The spectrum of the fully expanded hexyl-ammonium complex is included for comparison.

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two bands appear, one at 3680 cm^{-1} that represents the unperturbed OH groups and another at higher frequency that represents the OH groups that are interacting with the $-NH_3^+$ sitting above them. In the octyl-ammonium collapsed complex the second band appears at a higher frequency (3725 cm^{-1}) than in the fully expanded phase (3710 cm^{-1}). This indicates that the OH–NH_3 distance is shorter and, therefore, that the $-NH_3^+$ groups are sitting deeper in the hole than in the first case. Both adsorptions, the perturbed and the unperturbed, are observed only for inclined incidence which indicates that the OH groups are directed perpendicular to the layers. These results agree with those of the X-ray analysis by Johns and Sen Gupta (1967): in the collapsed complex, they found the nitrogen atom at 4·65 A from the center of the silicate layer and at 4·80 A for the fully expanded phase.

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Résumé—Deux complexes de vermiculute octyl-ammonium avec différentes périodicités de 001, ont été étudiés par la spectroscopie à l'infra-rouge. Dans chaque cas, la spectroscopie à l'infra-rouge fournit des renseignements sur l'orientation des groupes $—NH_3^+$ et la force du lien d'hydrogène entre ces groupes et les surfaces d'oxygène silicate. On a également observé une perturvation des groupes OH du silicate qui semble être en rapport avec la distance du centre du feuillet, à l'endroit où se trouvent les groupes $—NH_3^+$.

Les résultats infara-rouge sont discutés en fonction des modèles structuraux déduits de l'analyse aux rayons X.

Kurzreferat—Zwei Oktyl-Ammonium Vermiculit Komplexe mit verschiedenen 001 Periodizitäten wurden durch Infrarot Spektroskopie untersucht. In jedem Falle liefert die Infrarot Spektroskopie Auskunft über die Orientierung der $—NH_3^+$ Gruppen und die Stärke der Wasserstoffbindung zwischen diesen Gruppen und den Silikat Sauerstoff Oberflächen. Ferner wurde eine Störung der Vibration der OH Gruppen des Silikates beobachtet, die mit der Entfernung vom Mittelpunkt der Schicht an welcher sich die $-NH_3^+$ Gruppen befinden, zusammen zu hängen scheint.

Die Infrarot Ergebnisse werden im Zusammenhang mit den aus der Röntgenanalyse abgeleiteten Strukturmodellen erörtert.

Резюме—Методом инфракрасной спектроскопии изучены два октил-аммониевых комплекса вермикулита с различной периодичностью в направлении 001. Для каждого случая этот метод позволил получить информацию об ориентации групп NH_3^+ и интенсивности водородных связей между этими группами и кислородными поверхностями слоев. Кроме того наблюдались нарушения вибраций групп OH силиката, которые, очевидно, связаны с расстояниями, на которые группы NH_5^+ удалены от центров слоев.

Результаты ИКС—исследований обсуждаются с точки зрения структурных моделей, полученных с помощью рентгеновского анализа.

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